

Bi₂O₃ – GeO₂ GLASS AND TRANSPARENT GLASS CERAMIC BASED ON IT

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Translated from *Steklo i Keramika*, No. 2, pp. 11 – 15, February, 2011.

Glasses with the composition (in moles) 2Bi₂O₃, 3GeO₂ have been obtained. They have different color and electric properties. This is due to the different concentration of bismuth ions with degree of oxidation different from +3. The characteristic temperatures of these glasses have been determined, and on the basis of these temperatures heat-treatment regimes were chosen in order to obtain a transparent glass ceramic. The effect of the glassmaking regimes on the glass crystallization process is established. Some physical–chemical properties of the glass ceramic obtained have been investigated.

Key words: transparent glass ceramic, bismuth germanate, glass crystallization.

Glass technology is one of the most high-tech methods of producing widely used materials. However, ordinarily, single crystals play a considerable role. For example, germanium eulytine Bi₄Ge₃O₁₂ single crystals have found application as scintillators [1, 2] and, when doped with rare-earth ions, as a laser material [3]. Because of their disordered structure glasses are less suitable for such applications. In the mid-20th century crystal glass materials demonstrating fundamentally new applications as compared to glass were developed by directed crystallization of glass. Using this method, crystalline structures with a prescribed composition in the required amount can be developed. If the crystallites in the glass are sufficiently small, the material remains transparent and, possessing an ordered structure characteristic of single crystals will incorporate the properties of a single crystal and glass.

The existence of glasses in the system Bi₂O₃ – GeO₂ makes it possible to develop crystal glass material with a crystalline phase consisting of eulytine 2Bi₂O₃ · 3GeO₂ based on glass with the same composition. The task of the present work is to study the characteristics of the production and crystallization of glass with the composition presented.

Ultrapure Bi₂O₃ and GeO₂ calcined at 500°C were used as initial materials to produce the glass. The molar ratio of bismuth and germanium oxides was 2 : 3, which corresponds

to the eulytine composition. After weighing the powders were ground in an agate mortar to form a uniform mass. Preliminary sintering was conducted in a resistance furnace at temperature 700 – 720°C for several hours, periodically extracting and grinding the sinter. The prepared mix was melted in platinum crucibles at 1000 – 1100°C. At the completion of glassmaking the melt was poured onto a pre-cooled platinum foil. The quality of the glass was determined visually. When striae, bubbles, and other nonuniformities were present the glass was melted and re-poured.

A transparent glass ceramic was obtained by the widely used method of crystallizing glass under heat treatment, determining its characteristic temperature in advance by dilatometry (the rate of heating 3 – 4 K/min). Heat-treatment was conducted in a resistance furnace.

The refractive indices of the samples before and after heat treatment were measured by Lodochnik's method.

The phase composition of the samples was studied by x-ray phase analysis (DRON-3 x-ray diffractometer). The experimental data were analyzed and the phase composition of the samples was interpreted by means of the PCPDFWIN electronic catalogue.

The absorption spectra of the samples were recorded with a Shimadzu UV-3101 PC two-beam scanning spectrophotometer.

The electric properties of the glasses were measured with a “Meter L, C, R digital E7-12” instrument.

The scintillation characteristics of the samples were determined before and after heat-treatment. An I3-25-1 radiator was used to excite the luminescence, and an FÉU-39A photomultiplier, which possesses the highest sensitivity in the range 380 – 430 nm, was used to detect the radiation. The

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relative light emission efficiency was determined with a Ru-107 source.

Depending on the glassmaking conditions the color of the glasses changed, intensifying proportionally to the glassmaking time. After the melt was allowed to soak for 1.5 h dark red-brown glasses were obtained, and after a soaking time longer than 2 h the glasses darkened to such an extent that they lost their transparency. However, prolonged soaking of the melt at the glassmaking temperature is necessary to homogenize the melt.

On the basis of experimental and published data we have developed a method for obtaining samples of different color (from dark-red to light-yellow). The first step was soaking the melt at 1100°C for 1.5 h in order to homogenize it. To obtain dark-red glass a part of the melt was poured onto a substrate and dark glass was obtained (total glassmaking time 1.5 h). The remaining portion of the melt was also poured out onto a substrate, and once again the ingot obtained was placed into a crucible, inserted into a furnace cooled to room temperature, and gradually heated at the rate 300 K/h to the glassmaking temperature 1100°C. After allowing the melt to soak at this temperature for 10 min the glass samples poured off had a slightly yellowish color, and glass with a transitional orange color was obtained with repeated glassmaking for 40 min (it will be assumed in what follows that the duration of the glassmaking process for such glass is 10, 40 min, and so on, respectively, neglecting the duration of the first melt soaking). The results of the experiments show that the vaporization of the components of the melt has no effect on the color.

It is known that in complicated compounds containing bismuth oxide bismuth and ions in different oxidation states co-exist in a mobile state. It is this phenomenon that is responsible for the diverse color of the glasses [4]. For this reason it is important to understand whether or not the degree of oxidation of the bismuth ions changes during the glassmaking process; if yes, then it is important to know how the valence of bismuth changes relative to the stable degree of oxidation +3. In [5], devoted to the thermodynamic modeling of the system Bi–O, it is asserted that at sufficiently high temperatures of the order of 1000–1200°C oxide is stable with a lower degree of oxidation and Bi_2O_3 undergoes reduction to BiO. However, oxidation of bismuth can proceed in more complicated compounds. Thus, in the opinion of the authors of [6], heating of melt in the system Bi_2O_3 – GeO_2 results in the formation of the complexes $\text{Bi}_2\text{O}_3^{2+}$. It is asserted in [7] that pentavalent bismuth is always present in bismuth-containing systems in air and can replace germanium in tetrahedra. It is noted in [8] that, aside from Bi^{3+} , glass contains Bi^{5+} ions.

The authors of the present article are inclined to explain the change in the color of glass with prolonged homogenization of the melt in air precisely by the different concentration of bismuth ions with degree of oxidation above +3.

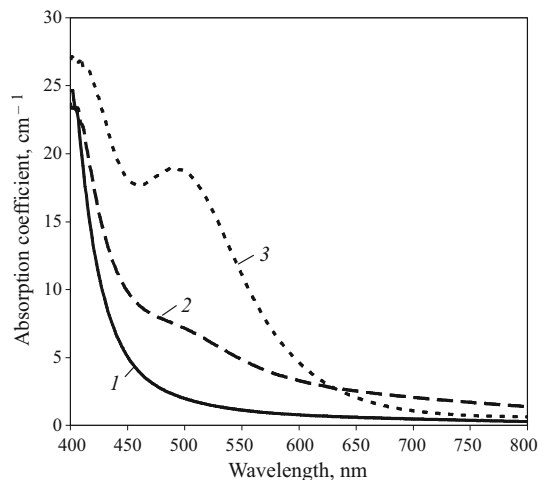


Fig. 1. Absorption spectrum of glasses with the composition (in moles) $2\text{Bi}_2\text{O}_3$, 3GeO_2 obtained with a long melt soaking duration: 1, 2, and 3) 10, 40, and 90 min, respectively.

During prolonged glassmaking, to all appearances oxidation of trivalent bismuth occurs in the melt at the first stage of glass preparation, which is what gives the dark color of the glass obtained by rapid cooling of such a melt. With rapid cooling of the melt the arising valence state freezes. The longer the soaking time of the melt, the darker are the glasses obtained and the higher the concentration of bismuth ions with degree of oxidation above +3. However, if dark glass is slowly heated at temperatures below the melting point, bismuth ions are reduced to oxidation degree +3, which results in fining of the glass. For short repeated soaking, there is not enough time for the melt to undergo oxidation, but for a long repeated glassmaking process the glass darkens once again.

An absorption band present in the range 460–500 nm and associated with the presence of bismuth whose degree of oxidation is higher than +3 is present in the absorption spectra of glasses having different colors. The intensity of the absorption band increases with increasing glassmaking time (Fig. 1).

Measurements of the resistivity and dielectric constant of glasses with different color confirm that it is precisely oxidative processes that occur in melt when making glass. The indicated temperature dependences for glasses with the composition (in moles) $2\text{Bi}_2\text{O}_3$, 3GeO_2 are presented in Figs. 2 and 3. According to [9] the electric properties of glasses with the composition (in moles) $2\text{Bi}_2\text{O}_3$, 3GeO_2 are determined by the ionic mechanism of conduction. It is evident from the curves displayed in Figs. 2 and 3 that not only the temperature but also the color of the glass affects the resistivity and the dielectric constant. For glasses with shorter making times and correspondingly a lighter color the conductivity is lower. Since the main charge carriers in bismuth-containing glass are oxygen ions, when bismuth undergoes oxidation in a long glassmaking process the carrier concentration increases, the

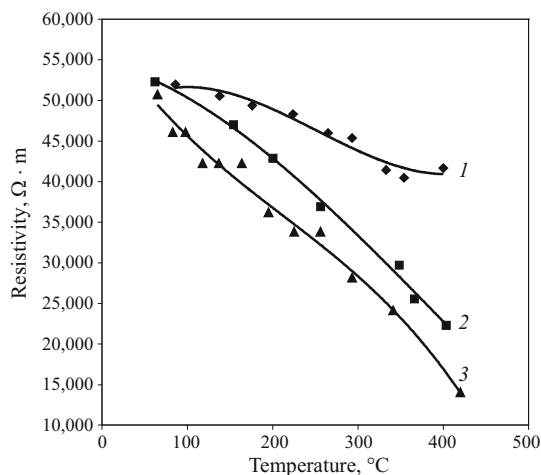


Fig. 2. Temperature dependence of the resistivity of glass with the composition (in moles) 2Bi₂O₃, 3GeO₂ obtained different soaking times of the melt: 1, 2, and 3) 15, 40, and 90 min, respectively.

conductivity increases, and the resistance decreases. The dielectric constant increases.

The interval of crystallization of the glasses obtained, which is determined by the dilatometric method, lies in the range 350 – 450 $^{\circ}C$ irrespective of the soaking time and color of the glass.

It was established that after glass is heat-treated at different temperatures the limiting values of the temperature interval of crystallization (350 \pm 10 and 450 \pm 10 $^{\circ}C$) are not optimal for heat treatment for purposes of obtaining a transparent glass ceramic, since at 350 \pm 10 $^{\circ}C$ crystallization proceeds very slowly while at 450 \pm 10 $^{\circ}C$ the phase δ -Bi₂O₃ starts to form and crystallization begins. This is accompanied by a sharp increase of the index of refraction, which is due to liquation and uncontrollable crystallization of the glass. For heat-treatment of glass, the temperature 420 \pm 10 $^{\circ}C$ was found to be best for obtaining a transparent glass ceramic.

Heat treatment of dark and light glasses for crystallization gives different results.

After heat treatment dark glasses (making time 90 min) darken even more strongly, and the absorption coefficient of the samples increases sharply (Fig. 4). Then clouding occurs and is followed by practically complete crystallization. The higher the temperature, the more intense these processes are.

Since no peaks of a crystalline phase are present in the x-ray diffraction patterns of clouded samples, we assume that the clouding is due to liquation of the glasses. Subsequent heat treatment leads to the crystallization of two phases which we identified as a phase with space group Fm3m and a metastable phase Bi₂O₃ · GeO₂.

Calculations showed that the Fm3m phase (two compounds crystallize in this space group — δ -Bi₂O₃ and BiO₂) has the same unit cell parameters as BiO₂. This also confirms our supposition that with prolonged soaking of the melt subsequent oxidation of bismuth occurs, and if the amount of

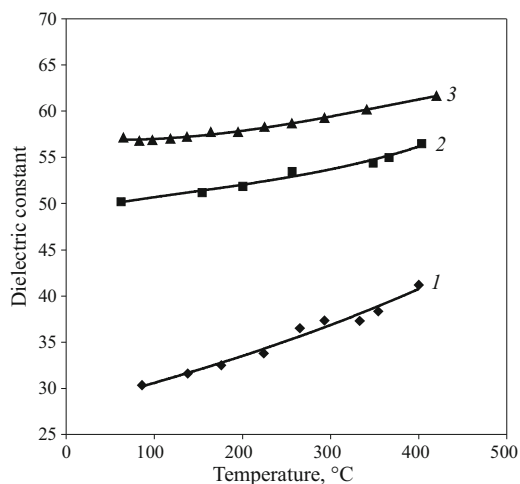


Fig. 3. Temperature dependence of the dielectric constant of glasses with the composition (in moles) 2Bi₂O₃, 3GeO₂ obtained with different soaking times of the melt.

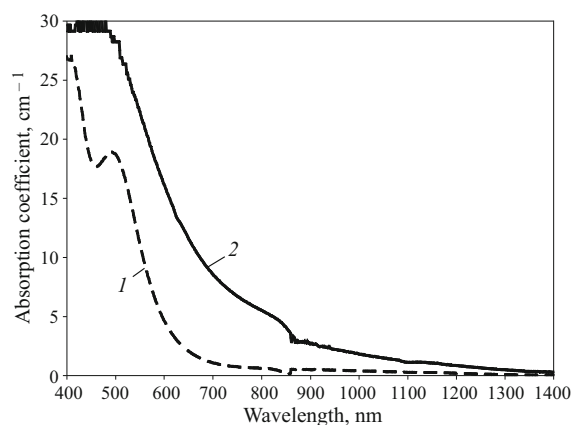


Fig. 4. Absorption spectrum of dark glass with the composition (in moles) 2Bi₂O₃, 3GeO₂ (making during 90 min) and the same glass after heat treatment: 1) no heat-treatment; 2) heat-treatment at 350 \pm 10 $^{\circ}C$ for 5 h.

bismuth with valence above +3 large, then subsequent heat-treatment leads to liquation and crystallization. Thus heat-treatment of dark glasses does not yield the required phase and the required optical transparency.

To obtain a transparent crystal glass material, light glasses were heat treated and their repeated glassmaking time was no longer than 1 h. The process of crystallization of such samples, unlike dark glasses, proceeds more slowly. Eulytine phase 2Bi₂O₃ · 3GeO₂ and the metastable phase Bi₂O₃ · GeO₂ crystallize in the process. As the heat-treatment time and temperature increase, the samples become visually even lighter, practically colorless, and their absorption coefficient decreases (Figs. 5 and 6). The content of the metastable phase also decreases. Hence it follows that soaking at temperatures much lower than the melting temperature results in reduction of bismuth to the initial degree of oxidation +3.

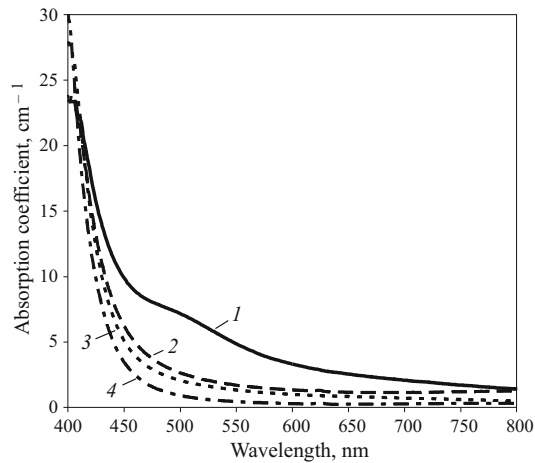


Fig. 5. Absorption spectra of glass with the composition (in moles) $2\text{Bi}_2\text{O}_3$, 3GeO_2 (making time 40 min) after heat-treatment: 1) no heat treatment; 2, 3, 4) after heat-treatment at $420 \pm 10^\circ\text{C}$ for 5, 10, and 20 h, respectively.

As the heat-treatment time and temperature increase, the refractive index of the crystal glass samples increases (Table 1) and becomes close to the index of refraction of a germanium eulytine single crystal (2.10 ± 0.02).

TABLE 1. Refractive Index of Samples with the Composition (in moles) $2\text{Bi}_2\text{O}_3$, 3GeO_2 (Making Time 40 min) after Heat-Treatment

Heat-treatment temperature, $^\circ\text{C}$	Heat-treatment time, h	Refractive index ± 0.02
No heat-treatment	—	1.88
350 ± 10	5	1.88
	10	1.92
390 ± 10	6	1.94
	9	1.95
420 ± 10	5	1.95
	10	2.00
	15	2.05
	20	2.08
450 ± 10	0.2	1.88
	1.2	1.92

TABLE 2. Volume Fraction of the Crystalline Phase and the Average Sizes of the Crystallites for Crystal Glass Materials Obtained with Heat-Treatment at $420 \pm 10^\circ\text{C}$ of Glasses with the Composition (in moles) $2\text{Bi}_2\text{O}_3$, 3GeO_2

Heat-treatment time, h	Volume fraction of the crystalline phase, %	Average sizes of the crystallites, nm
No heat-treatment	0	0
5	32	20
10	55	20
15	77	30
20	91	30

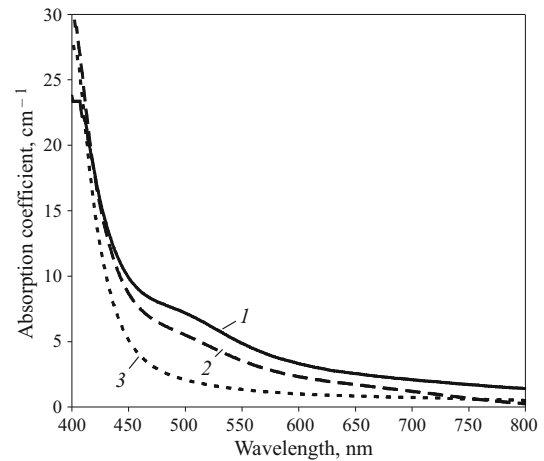


Fig. 6. Absorption spectra of glass with the composition (in moles) $2\text{Bi}_2\text{O}_3$, 3GeO_2 (making time 40 min) after heat-treatment for 10 h at different temperatures: 1) no heat treatment; 2) after heat-treatment at 350°C ; 3) after heat-treatment at 420°C .

For samples heat-treated at selected temperatures, the volume fraction of the crystalline phase was estimated on the basis of the values of the refractive indices. The XPA data were used to calculate (Scherrer equation) the approximate average sizes of the eulytine crystal (Table 2).

As one can see from Table 2, the volume fraction of the crystalline phase increases proportionally as the heat-treatment time, the sizes of the crystallites do not change, and the crystal glass material remains transparent.

Some basic scintillation characteristics were determined for samples of bismuth germanate glass and crystal glass (heat-treatment at $420 \pm 10^\circ\text{C}$ for 10 h). The results as compared with the characteristics of germanium eulytine single-crystals are presented in Table 3.

The main scintillation characteristics, such as the radiation length, the light yield, the emission time, and the interaction length of the crystal glass material obtained are much closer those of a single crystal than a glass with the corresponding composition.

TABLE 3. Scintillation Characteristics of Glass Samples with the Composition $2\text{Bi}_2\text{O}_3$, 3GeO_2 and Crystal Glass Material Based on It

Indicator	Glass	Glass ceramic	Single crystal germanium eulytine
Luminescence peak, nm	485	480	480
Luminescence decay time, * nsec	44	30	24
Radiative length, cm	1.3	1.15	1.1
Emission time, nsec	330	290	300
Light yield, % NaI	11	14	15
Interaction length, cm	24	22.3	21.8

* For wavelength 290 nm and 480 nm of the exciting radiation.

CONCLUSIONS

Bismuth with different degrees of oxidation can be present in glass. The concentration of the bismuth ions with oxidation degree greater than +3 depends on the soaking time of the melt at the glassmaking temperature.

Increasing the number of these ions results in darkening, a decrease and loss of transparency of the glasses, lowering the crystallization probability of the stable phase of eulytine.

The oxidation processes occurring during glassmaking likewise influence the electric properties of glass. For glasses subjected to longer making processes and correspondingly darker in color (glassmaking time 90 min) as compared with glass which underwent glassmaking for 10 min at the last stage, the value of the conductivity and dielectric constant are higher.

Heat treatment of samples of light glasses at a temperature much lower than the glassmaking temperature results in crystallization of the eulytine phase with an admixture of a metastable phase.

Dark glasses with a high concentration of bismuth ions with oxidation degree +3 darken under heat treatment, become cloudy as a result of liquation, and crystallize completely.

Thus, the color changes occurring in glass depending on the conditions of glassmaking and in glass ceramic during heat treatment are a consequence of reversible oxidation-reduction processes which proceed on melting, glassmaking, and subsequent heat-treatment of the glass.

The process of obtaining a transparent crystal glass material based on glass with the composition (in moles) 2Bi₂O₃, 3GeO₂ must be conducted in several steps: glassmaking with intermediate solidification of the melt, slow heating, melting and short-time soaking in a melted state; rapid cooling of the melt to obtain glass; long-time heat-treatment of the glass samples to attain crystallization. The volume fraction of the crystalline phase depends on the heat-treatment time but the crystallite sizes do not.

The physical–chemical and scintillation properties of the transparent crystal glass material obtained are close to those of a single crystal with the same composition. This makes it promising for use in a number of spheres where single crystals are usually used.

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